Life testing of $Yb_{14}MnSb_{11}$ for high performance thermoelectric couples

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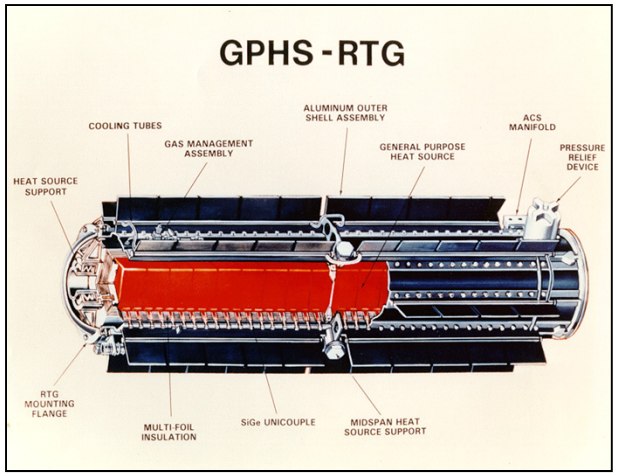
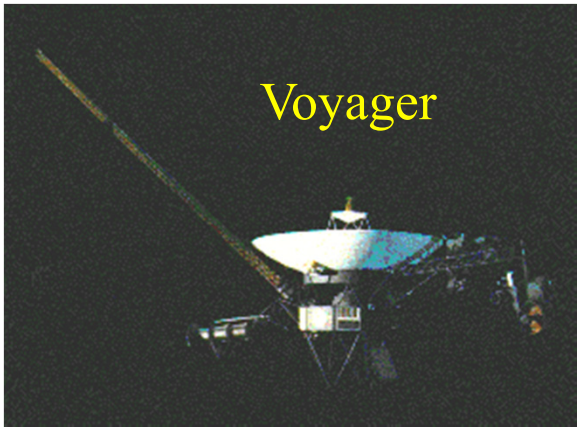
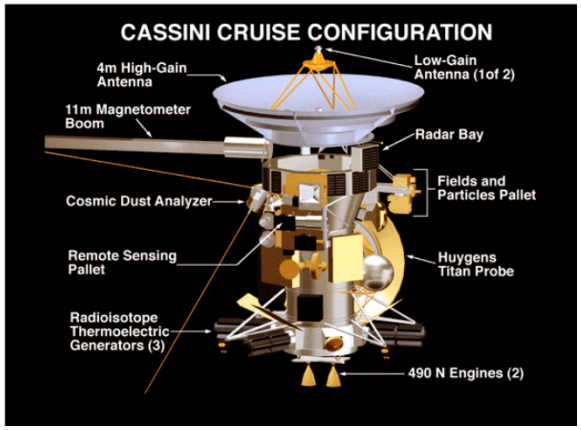
Outline

- **Introduction**
  - Thermoelectric materials and couples
  - Life verification for thermoelectric couples
  - Sublimation
- **Sublimation life test with $Yb_{14}MnSb_{11}$**
  - Development for sublimation suppression layer for $Yb_{14}MnSb_{11}$
  - Sublimation coupon test
- **Thermoelectric properties life test with $Yb_{14}MnSb_{11}$**
- **Contact resistance life test with $Yb_{14}MnSb_{11}$ /Mo/ $Yb_{14}MnSb_{11}$ coupon**
- **Summary**

Thermoelectric Materials and Device Technology



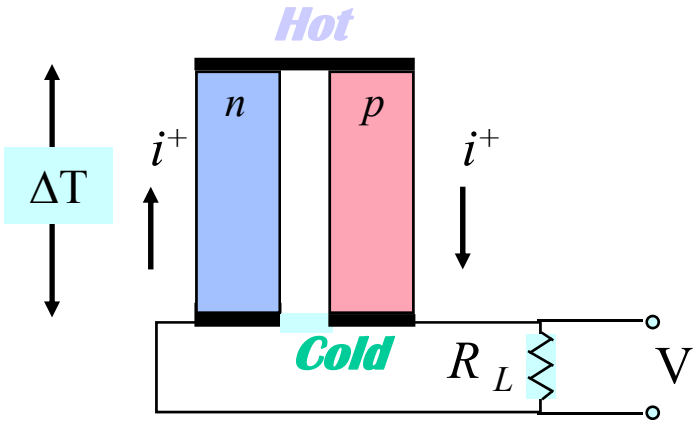




Mars Science Laboratory

- **Radioisotope Thermoelectric Generator**
  - **Used several deep space missions including Voyager and Cassini**
  - **Operated continuously more than 30 years**

Power generation



- **Thermal gradient leads to net diffusion of charge carriers to the cold side**
  - Hot charge carries move faster
  - Charge carriers diffused to the cold side
  - Charge is built up on the cold side
- **Seebeck voltage is established from thermal gradient**
  - V= αΔT
  - α is Seebeck coefficient
  - Convert heat to electricity

- **Efficiency of thermoelectric generator**

$$\eta = \frac{power\quad output}{heat\quad input} = \frac{\alpha^2 \sigma \Delta T^2}{\kappa \Delta T + \alpha T_h I - \frac{I^2 \rho}{2}}$$

- **Simplified efficiency**

$$\eta = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1+zT_{avg}} - 1}{\sqrt{1+zT_{avg}} + \frac{T_c}{T_h}}$$

- The efficiency becomes carnot efficiency ($\Delta T/T_h$) when zT goes to infinity.

$$\boxed{zT = \frac{\alpha^2 \sigma}{\lambda} T = \frac{\alpha^2}{\rho \lambda} T}$$

higher zT → higher efficiency

α= Seebeck coefficient, σ=electrical conductivity, ρ= electrical resistivity
T_h=hot side temperature, T_c=cold side temperature, $\Delta T = T_h - T_c$, $T_{avg} = (T_h + T_c)/2$
κ = thermal conductivity

Status of TE materials for high efficiency couples

	n-type Skutterudite	p-type Skuttrudite	$Yb_{14}MnSb_{11}$ (Zintl)	$La_{3-x}Te_4$
Maximum operating temperature	873K	873K	1273K	1273K
Average ZT			0.65 [1273 to 473K]	0.73 [1273 to 473K]
TE life test	In-progress	In-progress	Stable after 6 month aging at 1273K and 1323K	In-progress
Sublimation suppression	Demonstrated with aerogel (5×10^{-7} g/cm^2/hr for 6 months at 873K)	Demonstrated with aerogel (5×10^{-7} g/cm^2/hr for 6 months at 873K)	Demonstrated with alumina paste (2×10^{-6} g/cm^2/hr for 18 months at 1273K)	In-progress
Metallization			Stable after 1500 hr aging at 1273K	

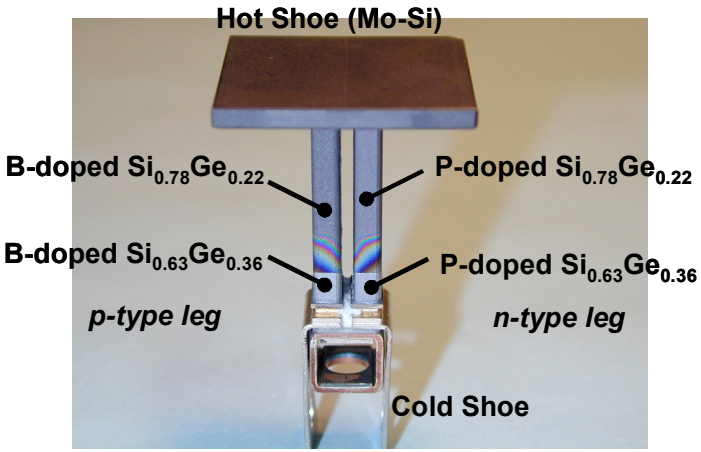
Comparison of TE couples

	N-PbTe	P-TAGS	N-RTG SiGe	P-RTG SiGe	N-nano-SiGe	P-Zintl	N-LaTe	P-Zintl	N-LaTe/ p-SKD	P-Zintl/ n-SKD
Average ZT	0.90	1.1	0.69	0.41	0.66	0.73	0.65	0.73	0.98	0.92
T_{max} (K)	800	675	1273	1273	1273	1273	1273	1273	1273	1273
Couple Efficiency	7.0% [800 to 485K]		7.5% [1273 to 575 K]		10.5% [1273 to 473 K]		10.2% [1273 to 473 K]		13.6% [1273 to 473 K]	
Application	MMRTG		GPHS-RTG		ARTG		ARTG		ARTG	

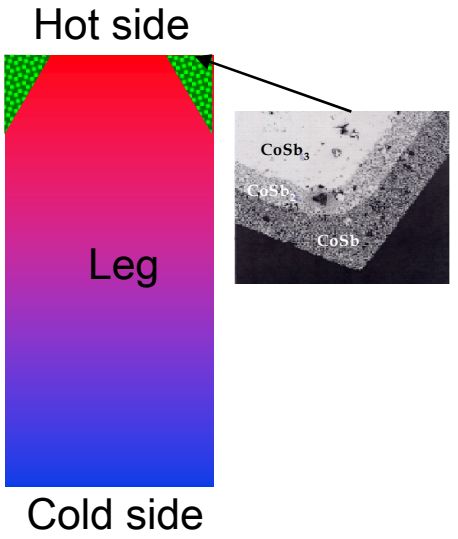
Life test for thermoelectric couples

- **Reason for life test**
  - **RTGs for deep space missions need to operate more than 10 years**
  - **Life test is required to verify the stability of thermoelectric couples**
- **Component life test**
  - **Preparing coupons and verifying stability of each component**
  - **Isolating each component**
  - **Subjects for component life test**
    - Thermoelectric properties of materials
    - Bonding interface
    - Sublimation
- **Coupon life test**
  - **Needed to verify the performance and stability with fabricated couples**

Sublimation phenomenon



GPHS RTG Si-Ge couple

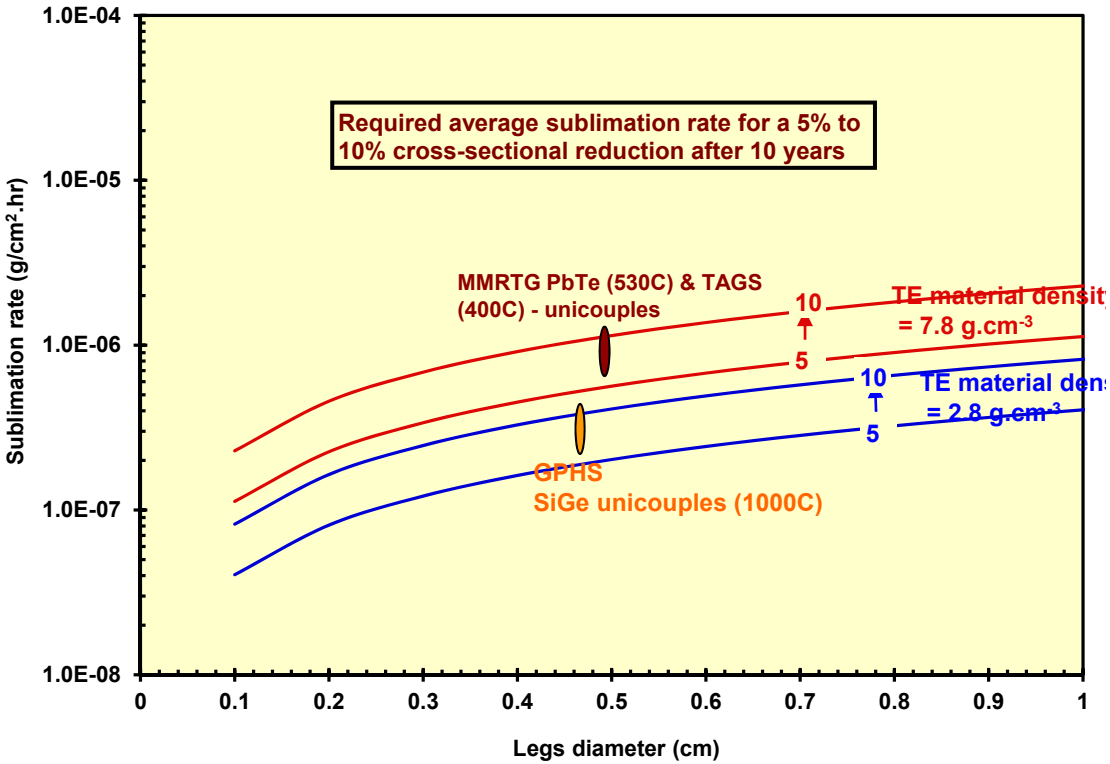


Sublimation phenomenon on a skutterudite leg

- **Most of TE materials used in power generation have peak figures of merit at the temperature where sublimation is significant.**
- **Sublimation leads to reduction of effective cross section, which leads to decrease in conversion efficiency**
- **Sublimed species can condense on cold side, which can cause short circuit on the device.**

Sublimation suppression

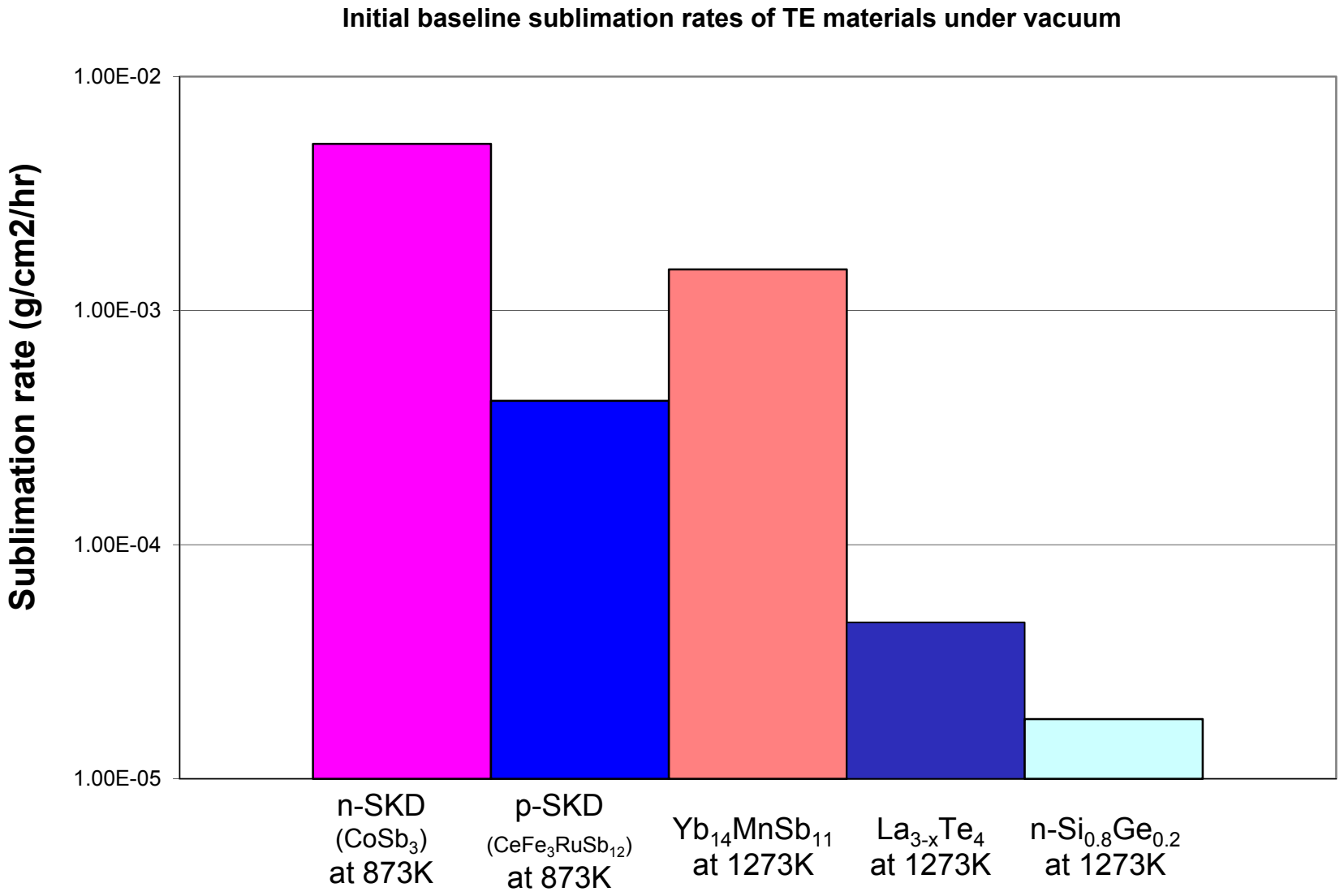
- **Sublimation suppression goal**
  - 5~10% effective cross sectional reduction after 14 years operation



- **Requirements for sublimation suppression barriers**
  - Chemical stability against TE materials
  - Thermal stability at the operating temperature
  - Withstanding stress during thermal cycling
  - No significant effect on system performance

- **Background on previous sublimation suppression methods**
  - SiGe RTG technology employed Si_3N_4/SiO_2 thin films
  - PbTe/TAGS technology employed an inert cover gas

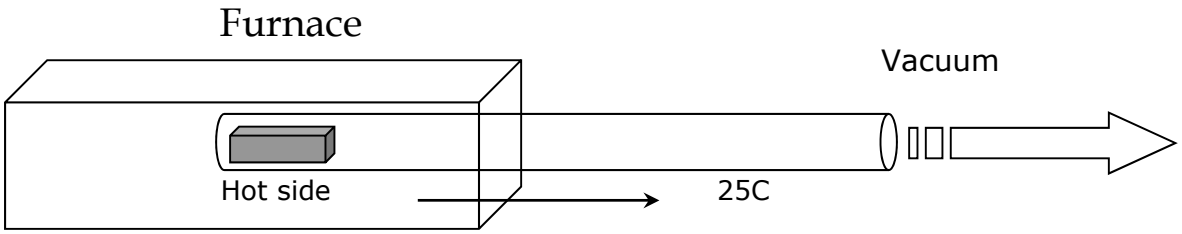
Beginning of life sublimation rate of TE materials in vacuum



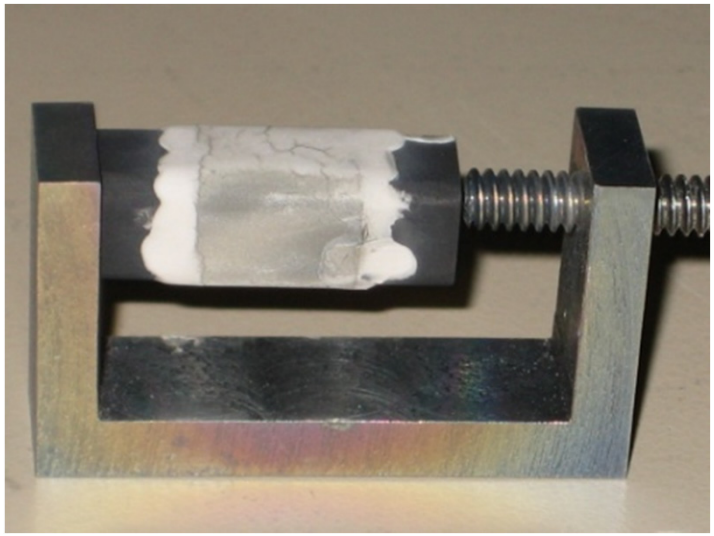
Development of sublimation suppression layer for $Yb_{14}MnSb_{11}$

- **Challenge**
  - High operating temperature (1273K)
  - Chemical reactivity
  - High CTE (~20 at 1273K)
  - High bare sublimation rate
- **Materials with limited reactivity against $Yb_{14}MnSb_{11}$ at 1273K**
  - Some refractory metals such as Mo, aluminum oxide, and carbon
- **Any candidate with matching CTE**
  - None
- **A way to alleviate CTE mismatch**
  - Adopting porous layer
- **Selected sublimation suppression barrier for $Yb_{14}MnSb_{11}$**
  - Porous aluminum oxide layer (commercial alumina paste from Cotronics)

Sublimation coupon test



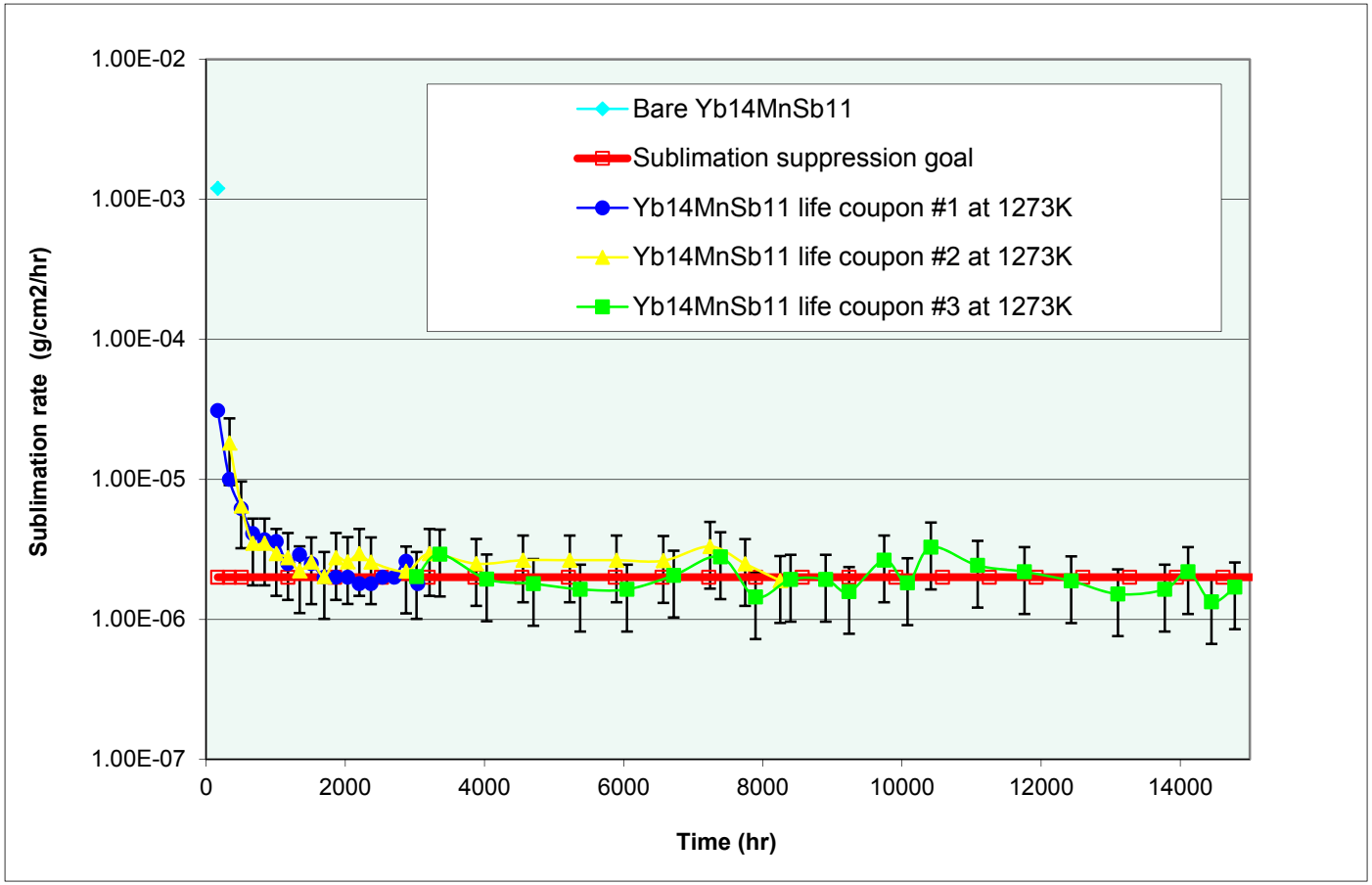
Sublimation test set-up



$Yb_{14}MnSb_{11}$ Sublimation coupon

- **Sublimation coupon preparation**
  - **Prepare a $Yb_{14}MnSb_{11}$ block**
  - **Prepare graphite blocks**
  - **Bond graphite blocks to the $Yb_{14}MnSb_{11}$ block using alumina paste**
  - **Apply alumina paste on the periphery of the $Yb_{14}MnSb_{11}$ block**
  - **Put the prepared assembly in a metallic clamp**
- **Sublimation test**
  - **Put the coupon into dynamic vacuum furnace and age desired period**
- **Sublimation rate measurement**
  - **Measure the weight change of the coupon before and after aging and calculate the sublimation rate**

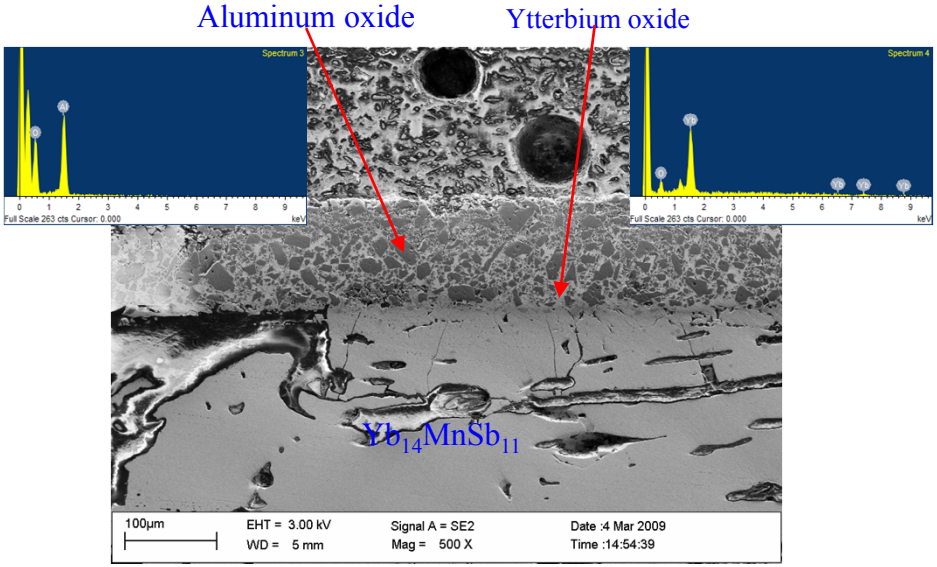
Sublimation life test with $Yb_{14}MnSb_{11}$ at 1273K



- **Sublimation rate continuously met the goal during 18 month coupon test**

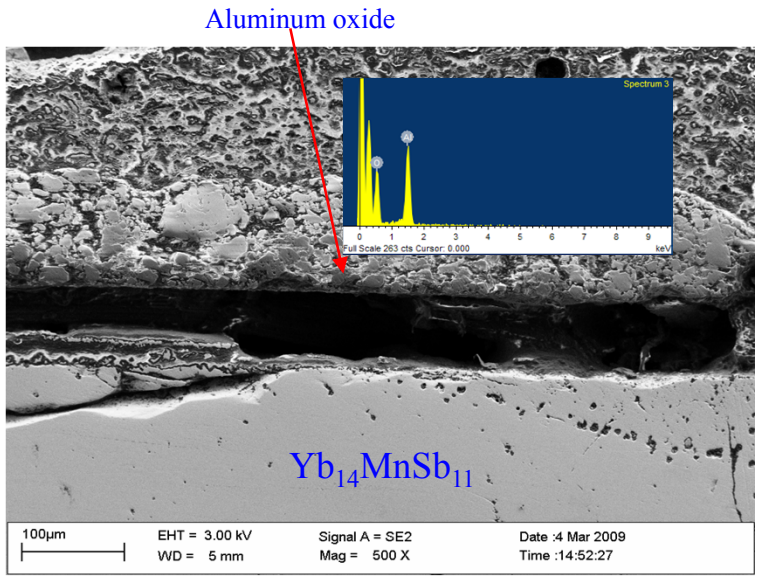
Clogging of alumina paste layer

Hot side (~1273K)

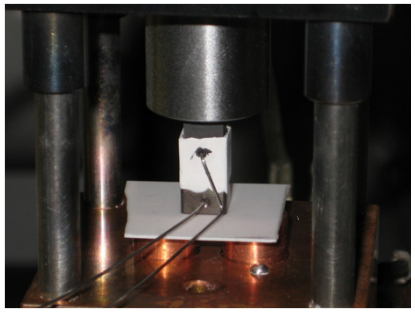


- Hot side SEM image shows clogging of alumina paste layer with ytterbia after 1500 hr in-gradient test

Cold side (~773K)

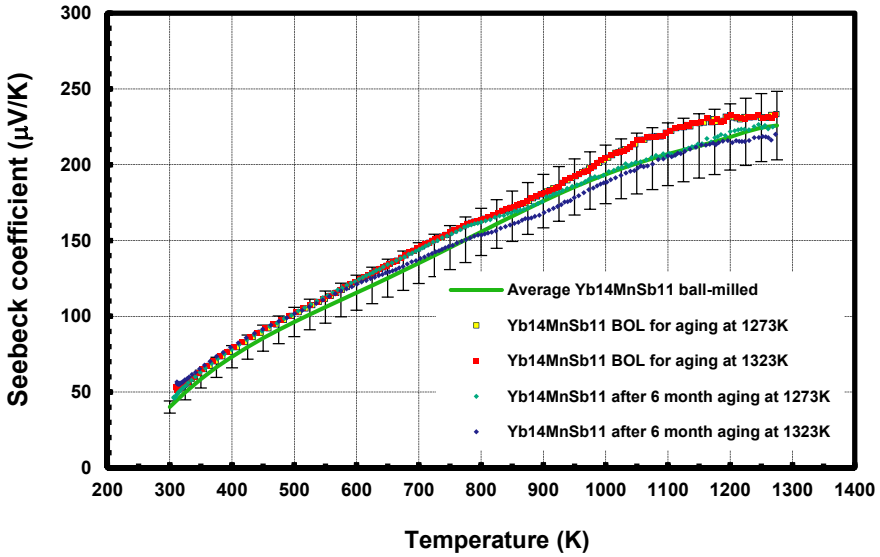


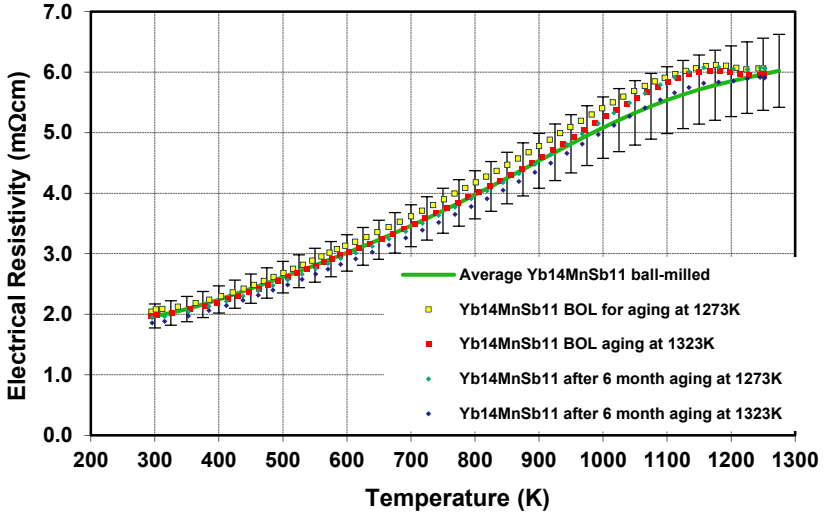
- Cold side SEM image shows no clogging of alumina paste layer



In-gradient test set-up

TE properties life test with $Yb_{14}MnSb_{11}$





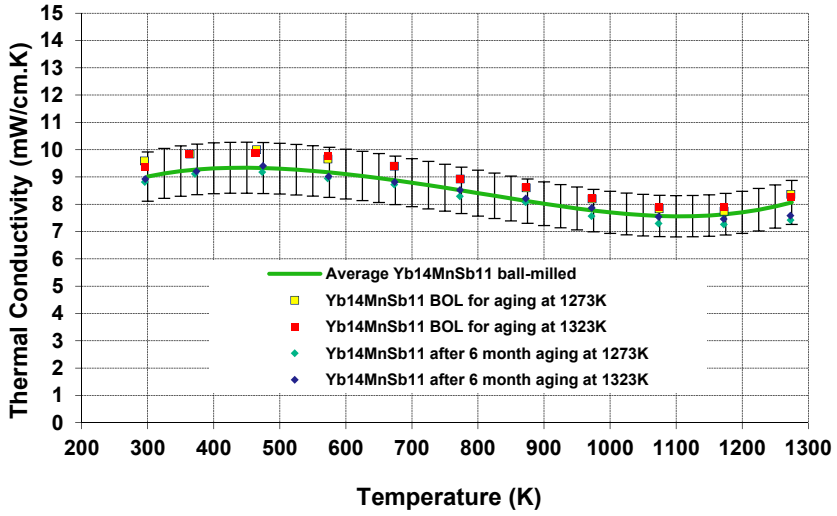
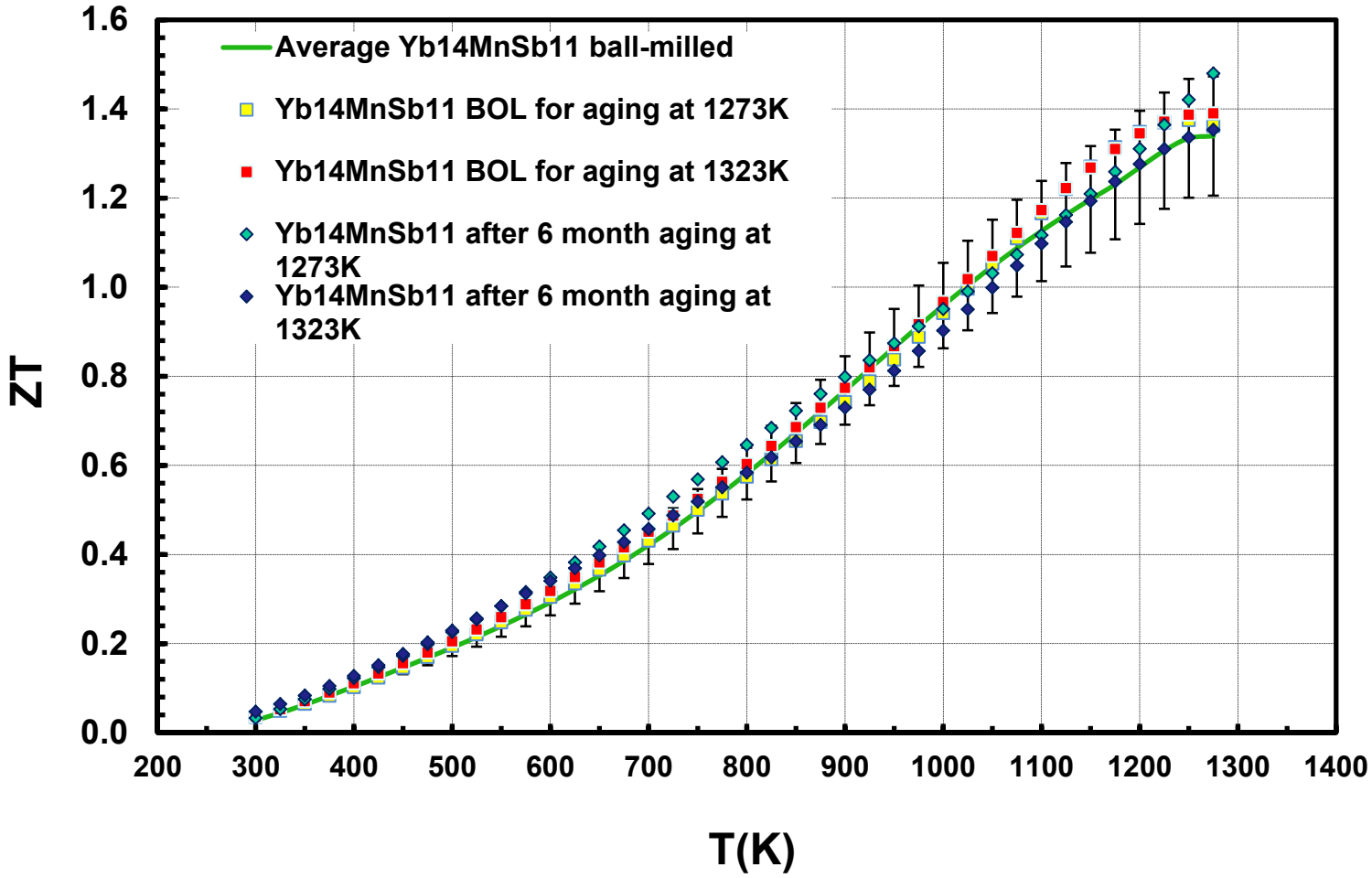
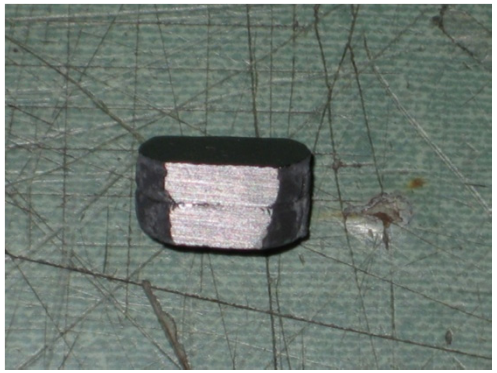


Figure of merit of $Yb_{14}MnSb_{11}$

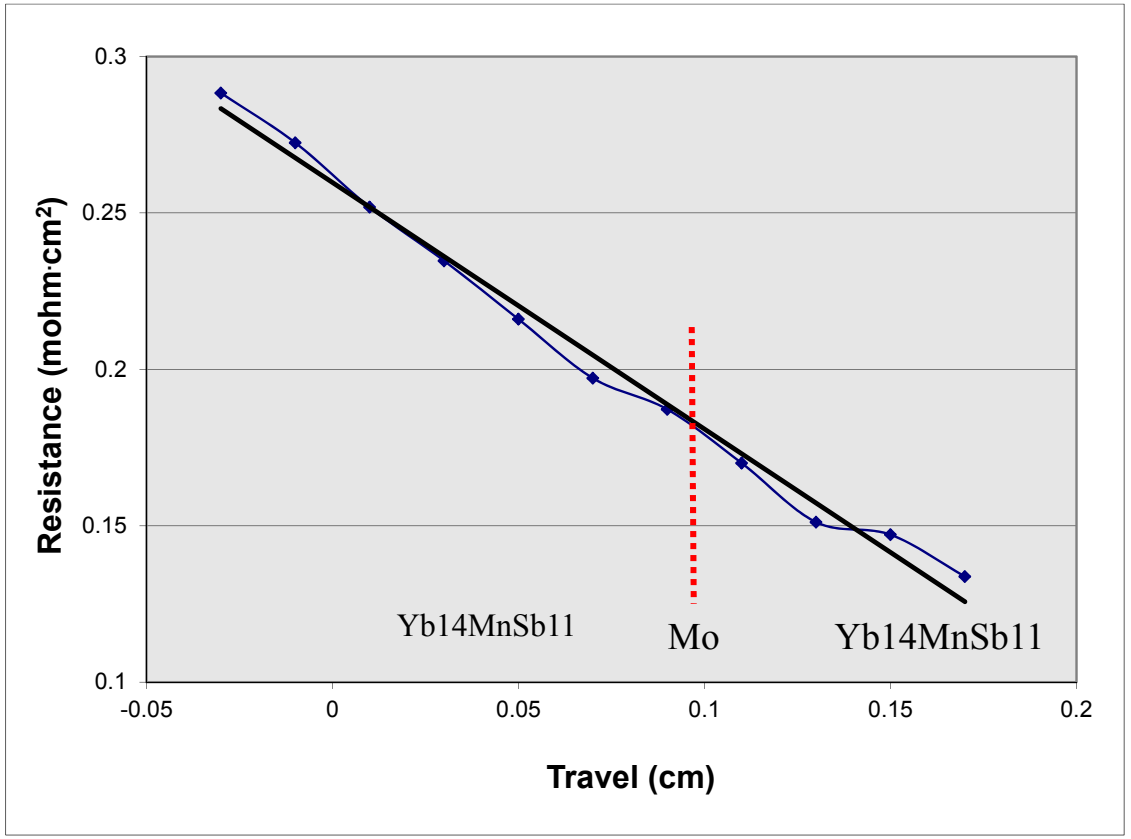


- There is no degradation on TE properties of $Yb_{14}MnSb_{11}$ after 6 month aging at either 1273K or 1323K.

$Yb_{14}MnSb_{11}$/Mo/$Yb_{14}MnSb_{11}$ Contact Resistance Life Testing after 1500 hr aging at 1273K



$Yb_{14}MnSb_{11}$/Mo/$Yb_{14}MnSb_{11}$ coupon after 1500 hr aging at 1273K



- A $Yb_{14}MnSb_{11}$/Mo/$Yb_{14}MnSb_{11}$ coupon showed no measurable contact resistance after 1500 hr at 1273K.

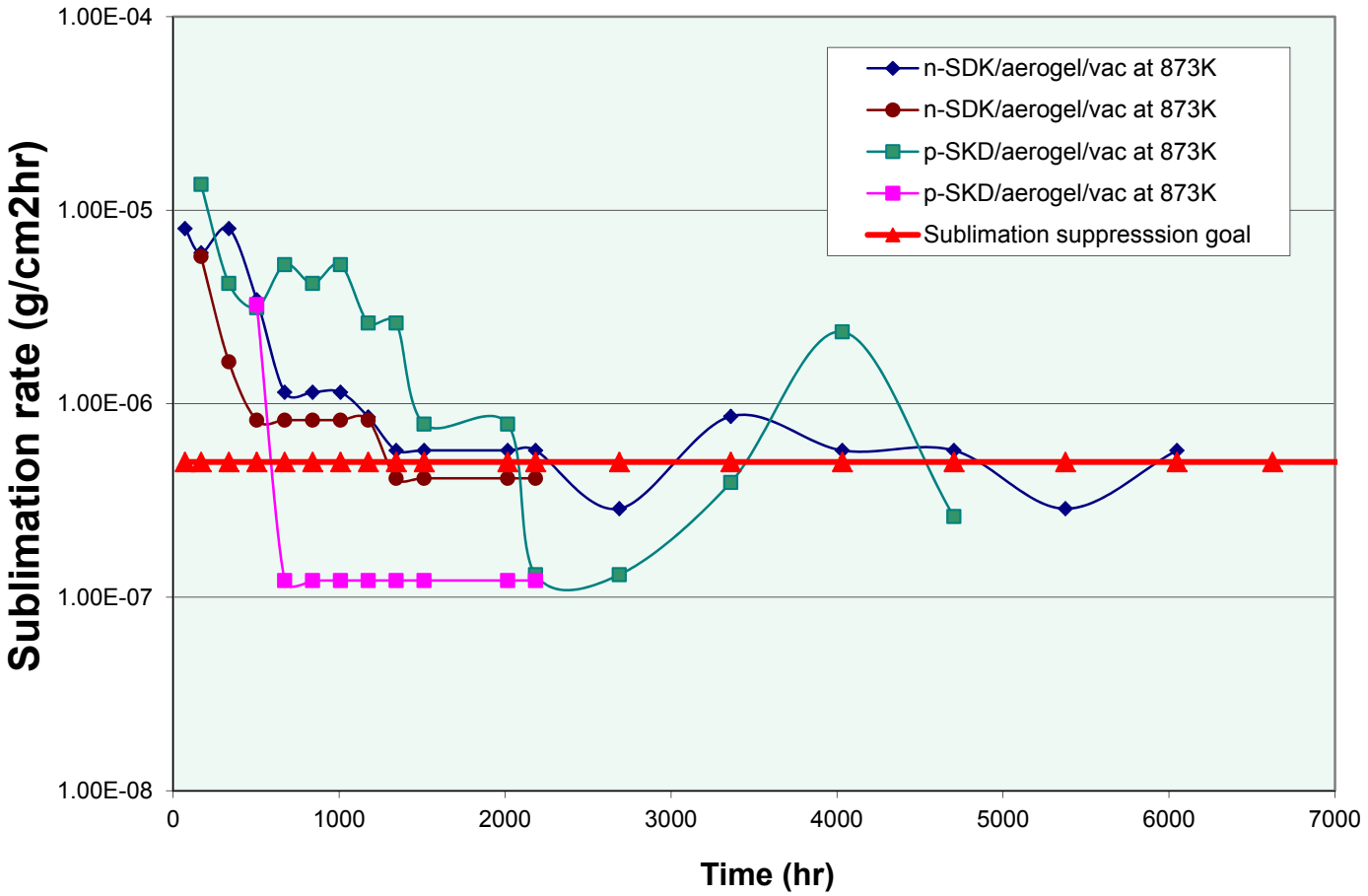
Summary

- TE properties of $Yb_{14}MnSb_{11}$ was maintained after 6 month aging at 1273K or 1323K (no degradation).
- Stable sublimation suppression layer for $Yb_{14}MnSb_{11}$ has been developed.
- Sublimation life test with $Yb_{14}MnSb_{11}$ coupons demonstrated that sublimation suppression goal has been met continuously for 18 months.
- The contact resistance between the Mo metallization and the $Yb_{14}MnSb_{11}$ remained negligible after 1500hr of aging at 1273K
- These life test results successfully demonstrated that $Yb_{14}MnSb_{11}$ can be incorporated into high efficiency thermoelectric couples
- Couple test is currently conducted.

Acknowledgements

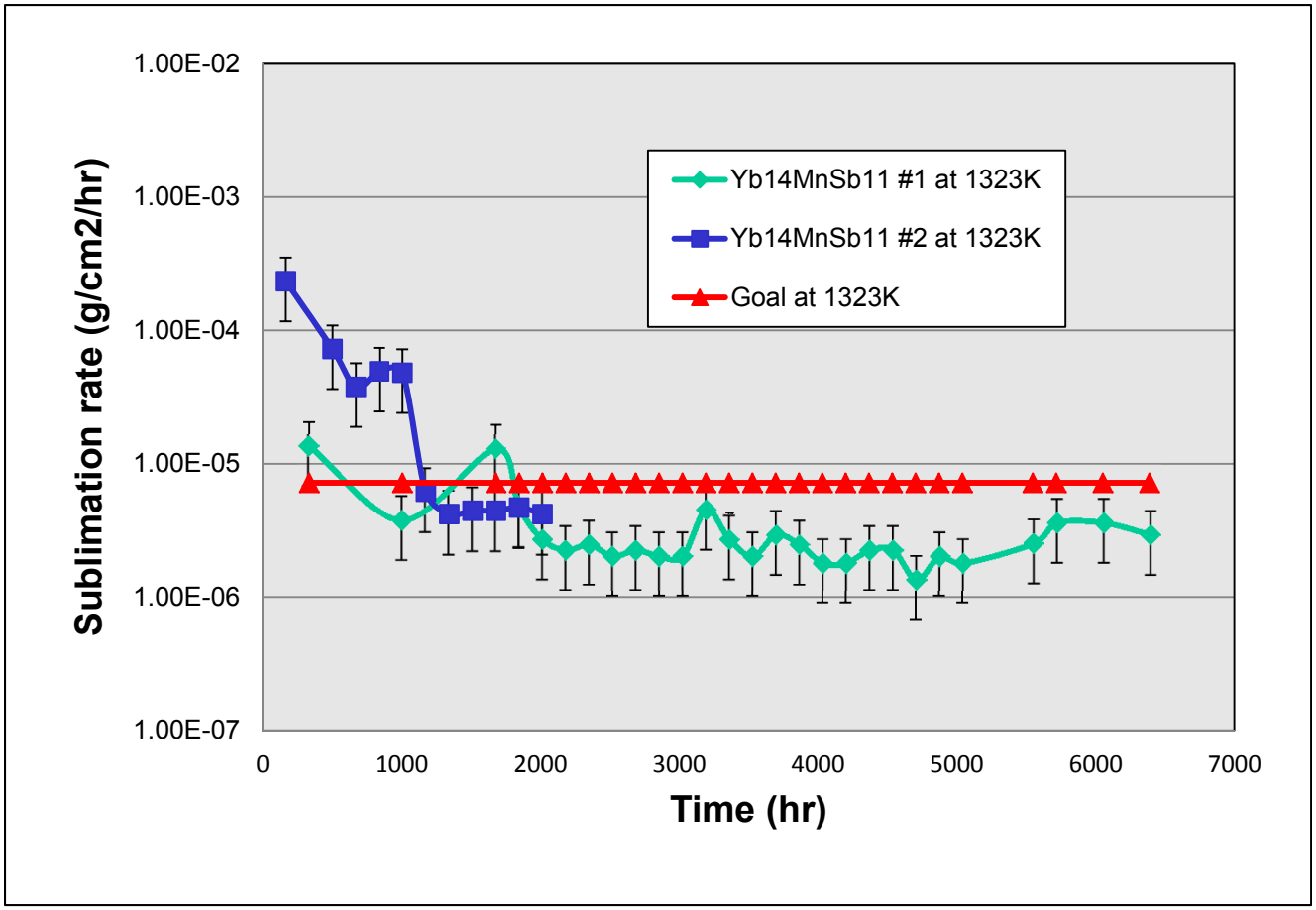
- **Chen Kou Huang**
  - providing $Yb_{14}MnSb_{11}$
- **Billy Chun-Yip Li**
  - providing metallized $Yb_{14}MnSb_{11}$ coupons
- **George Nakatsukasa and Leslie D. Zoltan**
  - measuring high temperature thermoelectric properties

Sublimation life test with n-SKD at 873K



- **Sublimation of skutterudites was successfully suppressed with aerogel**

Sublimation life test with $Yb_{14}MnSb_{11}$ at 1323K



- **Accelerated test at 1323K also confirmed sublimation suppression of $Yb_{14}MnSb_{11}$ with alumina paste layer**

Estimated sublimation rate through aerogel

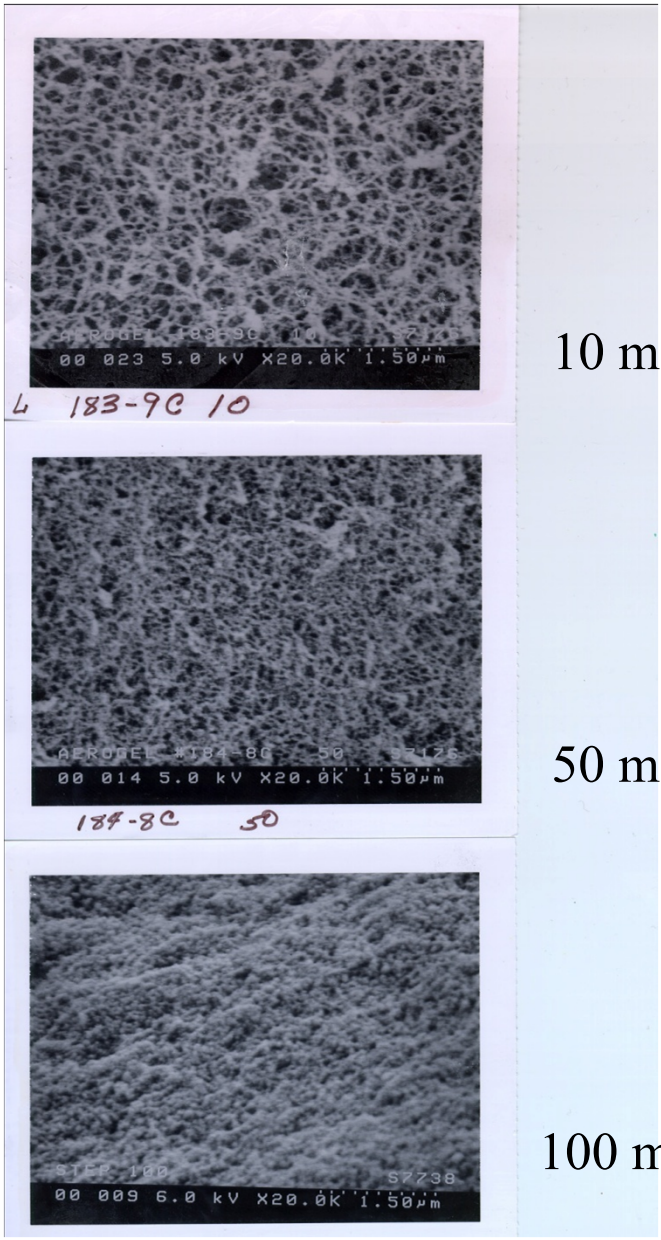
Flux through porous media

$$J = \frac{2}{3} d \frac{\varepsilon}{\tau} \sqrt{\frac{8RT}{\pi M}} \frac{dC}{dx}$$

J=Flux, d=pore diameter of porous media, ε= porosity, τ=totuosity, R=8.314 J/mol·K, T=temperature, M=Molecular weight, C=concentration, *x*=distance

- **If d = 50 nm, density of aerogel = 200 mg/cc, and *x* = 5 mm, estimated sublimation rate of Sb through aerogel at 700C is ~5.85×10^{-7} g/cm^{2}hr.**

- **Aerogel is expected to show better sublimation suppression property with increasing density.**
  - **Average pore diameter decreases with increasing density**



10 mg/cc

50 mg/cc

100 mg/cc